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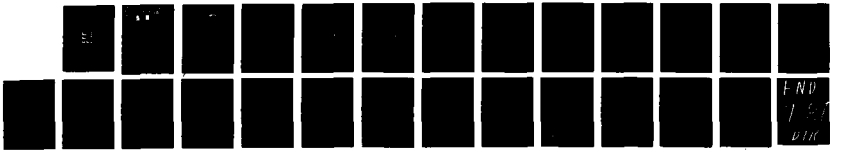

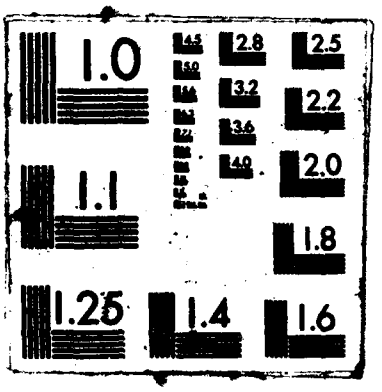
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Spectroscopic and Magnetic Studies of Two Electrically Conducting Charge Transfer Compounds of 7,7,8,8-Tetracyanoquinodimethanide with Cationic Copper Chelates

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Abstract

Electronic spectral data for $[Cu(en)_2][TCNQ]_2$ reveal a $TCNQ^- + TCNQ^- \rightarrow TCNQ^0 + TCNQ^{2-}$ charge transfer band at 1220 nm. Using a value for the transfer integral t of 0.2, then a value for the Coulomb integral U of 1.3 eV may be estimated from the relationship $\Delta E(CT) = (U - \sqrt{2}t)$. A band gap is expected to open at the Fermi level for values of $4t/U < 1.15$, and ΔE_{ST} is estimated to be 0.12 eV from the relationship $\Delta E_{ST} = 4t^2/U$. The lack of a contribution of paramagnetism from $TCNQ^-$ to that of $[Cu(en)_2][TCNQ]_2$ may be understood, even in the absence of charge transfer, since a system with ΔE_{ST} of 0.12 eV would exhibit a magnetic susceptibility of 10^{-5}emu/mole at 300 K. This small magnetic susceptibility can not be detected in the presence of the molar magnetic susceptibility of

$[Cu(en)_2][TCNQ]_2$. In addition to the $TCNQ^- + TCNQ^- \rightarrow TCNQ^0 + TCNQ^{2-}$ CT band, $[Cu(phen)_2][TCNQ]_2$ exhibits a $TCNQ^- + TCNQ^0 \rightarrow TCNQ^0 + TCNQ^-$ band at 2500 nm. The magnetic susceptibility of $[Cu(phen)_2][TCNQ]_2$ indicates that, on the average, one-third to one-half an electron is transferred from each $TCNQ^-$ site to $[Cu(phen)_2]^{2+}$, and the site preference energy $\underline{E}$ is 0.17 to 0.25 eV. Since $\underline{E}$ and $\underline{t}$ are comparable in magnitude, the bandwidth is appreciable, and high electrical conductivities and low activation energies are expected, and observed.

Introduction

In the initial work on charge transfer compounds of 7,7,8,8,-tetracyanoquinodimethanides, Melby et al. reported several compounds with copper chelates that had relatively high electrical conductivities. One of the advantages of using copper(II) chelates as acceptors in charge transfer compounds with $TCNQ^-$ would appear to be the high probability of forming stacked $TCNQ^-$ segarated chains in preference to mixed CuL_2^n-TCNQ stacked chains. The cationic copper chelate-TCNQ charge transfer compounds have unusual properties and have continued to attract attention.[2-6] For example, Hoffmann, et al.[2] found an exocyclic sigma-bonded TCNQ dimer in $[Cu(2,9\text{-dmphen})_2^n]_2^n[TCNQ]_2^n$ (2,9-dmphen = 2,9-dimethyl-1,10-phenanthroline) and were able to characterize the excited state arising from homolytic breaking of the sigma bond. Recently, Inoue and Inoue[6] have found that $Cu(dpa)_2(TCNQ)_2$ (dpa = di-2-pyridiylamine) exhibits metal-like

conductivity. This significant finding has stimulated additional studies on TCNQ salts with copper chelates since an understanding of electron-transport properties may lead to the production of a variety of new metal-like materials. Results of our studies of the electronic structural properties of the compounds $[CuL_2^{\pi}][TCNQ]_2^{\pi}$ (L = ethylenediamine or 1,10-phenanthroline) are reported in this article.

Experimental

Synthesis. In a typical preparation, approximately 0.1 mmol of the appropriate copper(II) salt, either $[Cu(phen)_2][NO_3]_2$ or $[Cu(en)_2][NO_3]_2$, was dissolved in 50 mL of distilled water. This solution was filtered and deaerated by bubbling with N_2 or Ar for approximately 20 min. While stirring this solution under an inert atmosphere, a solution of 0.2 mmol of LiTCNQ in 50 mL distilled, deaerated water was added slowly in a Schlenk filter apparatus. A precipitate formed immediately. After addition was complete (approximately 15-20 min) the solution was stirred for another 15 min, and the precipitate was collected on a glass frit and was washed with a small amount of distilled water. The fine powders were then dried under vacuum at room temperature. The samples were stored under vacuum until used.

$[Cu(phen)_2][TCNQ]_2$ was collected as a black powder. Anal. Calcd for $CuC_{48}H_{24}N_{12}$: C, 69.23; H, 2.91; N, 20.20. Found: C, 68.84; H, 2.90; N, 20.29.

$[Cu(en)_2][TCNQ]_2$ was collected as a dark purple powder. Anal. Calcd for $CuC_{28}H_{24}N_{12}$: C, 56.78; H, 4.09; N, 28.38. Found: C, 56.95; H, 4.24; N, 28.18.

Electronic Spectral Measurements. Solid state electronic absorption spectra were obtained by using powdered samples mixed with IR grade KBr and pressed into pellets.[7] Dilute mixtures on the order of 1 mg of sample per 300 mg of KBr were used. The possibility of solid state reactions was ruled out because pellets pressed for only a few minutes and pellets pressed for 5 hrs had identical spectra. The results were completely reproducible. EPR spectra of crushed pellets showed no changes when compared with spectra taken of the samples simply mixed with KBr. Spectra were obtained at 77 K by using a Cary 17I spectrophotometer and a liquid dewar.

Electron Paramagnetic Resonance. EPR spectra at X-band were obtained by using a Varian E-109 spectrometer system. The magnetic field was calibrated with a DPPH marker, and the frequency was monitored with a Hewlett-Packard 5245L frequency counter. Powder spectra were obtained at room and liquid-nitrogen temperatures.

Magnetic Susceptibility Measurements. Magnetic susceptibility data were obtained by using a Faraday balance system consisting of a Cahn 2000 electrobalance, an ANAC Series 3472 100 mm electromagnet equipped with an ANAC magnet control system and powered by a Sorenson SRL 40-50 power supply. The field gradient was provided by a set of Lewis coils (George Associates, model 502) which were powered by a Georges Associates bipolar, current regulated, power source (model

202). Approximately 10-20 mg of sample was used. Samples were contained in a small quartz bucket, which was obtained from Ruska Instrument Co., and which was suspended from the balance by using quartz fibers. The field used was approximately 7 KG, and the gradient was $\pm$160 G/cm. The balance was calibrated with $HgCo(NCS)_4$[8] and with Gd_2O_3.[9] The measurements were carried out in a helium atmosphere.

For low temperature data collection, a small dewar filled with $N_2(l)$ was placed around the sample tube and the sample was allowed to warm slowly to room temperature. The temperature was monitored constantly, and data were typically collected at intervals of two degrees. The sample temperature was measured by using a Lake Shore Cryotronics, Inc. DT-500 Si diode and DRC-80C temperature controller. The diode was placed slightly below the sample bucket inside the sample tube. Data were collected automatically using a Hewlett-Packard 3495A scanner, a Fluke 8520A digital multimeter, and a Tektronix 4052 computer.

For high temperature data collection, a heating tape was wrapped around the sample tube, and the temperature was controlled manually by using a Variac. Temperatures were measured with a Pt resistor, which was placed in the sample tube below the sample bucket. A Fluke 8600A digital multimeter interfaced to the Tektronix 4052 computer via a Fluke 1120A translator was used to collect temperature data.

A value of -1.21×10^{-4} emu mol^{-1} was used as the diamagnetic correction for TCNQ,[10] Pascal's constants were used for the

estimation of diamagnetic corrections for the other components,[8] and a value of 60×10^{-6} emu mol^{-1} was applied to account for the second order Zeeman effect of copper(II).

Results

Electronic Spectra. Electronic spectral data for $[Cu(en)_2][TCNQ]_2$ and $[Cu(phen)_2][TCNQ]_2$ along with assignments, based on literature precedents, are given in Table I. The electronic absorption spectrum of $[Cu(en)_2][TCNQ]_2$ exhibits three major bands. The most intense band occurs at 365 nm, and two additional intense bands occur at 617 and 1220 nm, respectively. The lower energy band is very broad with a width at the baseline of approximately 600 nm. At 77 K, this absorption band becomes more intense and slightly more narrow. Upon cooling to 77 K, the two high energy bands are blue shifted by 10 and 5 nm, respectively, and both bands increase in intensity. In addition, at 77 K, shoulders of low intensity appear at approximately 660 nm, 570 nm, and 380 nm, and a new, low intensity band appears at 850 nm.

The most intense band in the spectrum of $[Cu(phen)_2][TCNQ]_2$ occurs at 370 nm with there being a second intense band at 875 cm^{-1}, and a very broad band of low intensity centered at approximately 2500 nm. At 77 K, a shoulder at 410-420 nm appears on the 370 nm band, and the 875 nm band is blue shifted to 870 nm. In addition, at room temperature there are spectral features at approximately 1000 nm and 1170 nm. While the 1000 nm shoulder is blue shifted to 980-990 nm at

77 K, the position of 1170 nm band does not change. Additional spectral bands of low intensity are given in Table I.

Features in the electronic spectra of the $[Cu(L)_2][TCNQ]_2$ compounds may be understood in terms of the electronic structures of $[TCNQ]_n^{q-}$ (q = 0, 1, 2; n = 1, 2). The spectral features probably arise from transitions at defects and chain ends, and from $TCNQ^- + TCNQ^- \rightarrow TCNQ^0 + TCNQ^{2-}$ and $TCNQ^- + TCNQ^0 \rightarrow TCNQ^0 + TCNQ^{2-}$ charge transfer. These latter features are the broad bands in the near infrared. Although there is no direct evidence of stacking of TCNQ molecules and ions to form chains, the magnetic data presented below provide evidence of strong interactions between TCNQ units, and the relatively high electrical conductivities suggest delocalization.

An SCF-LCAO-MO calculation of $TCNQ^-$ by Lowitz[11] provides the essential features necessary to understand the absorption spectrum of isolated $TCNQ^-$. The highest occupied molecular orbitals is a singly occupied $3b_{2g}$ giving a $^2B_{2g}$ ground state. The lowest lying excited state, $^2B_{1u}$, has the configuration $(3b_{1u})^1(3b_{2g})^2$, and the next higher excited state, ^2A_u, has configuration $(3b_{1u})^2(2a_{1u})^1$. Transitions to these states are expected to occur at 730-830 nm and 385-415 nm, respectively. More sophisticated calculations, such as that by Jonkman and Kommandeur,[12] which involved configuration interaction, support the spectral assignments and predicted energy ranges.

Magnetic Susceptibility. Magnetic susceptibility data for $[Cu(en)_2][TCNQ]_2$ and $[Cu(phen)_2][TCNQ]$ are presented in Figures 1 and

2, respectively. Where there is overlap, the magnetic data are in good agreement with the data reported by Inoue and coworkers.[4] The magnetic susceptibility data for $[Cu(en)_2][TCNQ]_2$ may be fit by the Curie-Weiss law with S = 1/2, g = 2.10, and θ = 8.32. Since contributions from $TCNQ^-$ molecules are not necessary to explain the observed data, it may be concluded that the $TCNQ^-$ molecules are strongly coupled magnetically. Interactions between the TCNQ molecules and the copper(II) complex cations would be reflected in the magnetic behavior, and since S = 1/2 behavior was found, such interactions are also absent. The magnitudes of the magnetic susceptibility and effective magnetic moment indicate that a negligible amount of electron transfer has occurred from the $TCNQ^-$ molecules to the copper(II) complex cations.

In the treatment of the data for $[Cu(phen)_2][TCNQ]_2$, the system was assumed to consist of copper(I) and copper(II) complex cations and $TCNQ^0$ and $TCNQ^-$ molecules within clusters or chains. The low values for the magnetic susceptibilities and magnetic moments indicate that a substantial amount of electron transfer has occurred and that a large percentage of the copper complex cations are in the copper(I) state.

If there is site preference for the electrons on the TCNQ chain, then the cluster models may be appropriate for the description of the magnetic susceptibility. The simplest cluster model consists of a pair, and the appropriate equation for the magnetic susceptibility is

$$X = 2(p - 0.5)\cdot(C/T) + p\cdot \frac{2N\mu_B g^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]$$

where the first term is the Curie contribution of the copper(II) complex cations, C is the Curie constant, and p is the degree of band filling. A p value of 1 indicates a 1/2 filled band, and a p value of 0.5 indicates a 1/4 filled band. The quantity $2(p - 0.5)$ represents the fraction of copper(II) in the sample. The g value in the first term was held constant at the experimental value of 2.07. The second term is the contribution from the TCNQ clusters (pairs) with an energy gap of $2J = \triangle E_{ST}$. The g value was taken to be 2.0 for the organic radicals. The exchange coupling constant is given by the following expression:[13]

$$J = \left[\frac{t^2}{U + (4t/\pi)\sin\pi p}\right]\left[1 - \frac{\sin 2\pi p}{2\pi p}\right]$$

where $\underline{U}$ and $\underline{t}$ are Coulomb and transfer integrals, which are defined in the Discussion section.

This model was applied and as shown in Figure 2, a reasonably good fit to the data was obtained with $p = 0.71$ and $2J = -0.077$ eV (620 cm^{-1}, singlet ground state). It is possible that the fit could be improved by assuming a distribution of cluster sizes, but the number of parameters would also increase. Calculations using a distribution of clusters were not attempted.

The magnetic susceptibility equations were fitted to the experimental magnetic susceptibility data by using a Simplex non-

linear least squares fitting program[14] with the criterion of best fit being the minimum value of the function

$$F = \sum_i [(\chi_M^{obs} - \chi_M^{calc})]^2/[\chi_M^{obs}]^2$$

Discussion

The experimental results suggest strong intermolecular interactions between the TCNQ molecules in both copper complexes. If these molecules stack to form chains, as is common in TCNQ charge transfer compounds, then strong intermolecular interactions may not be confined to pairs of TCNQ molecules. Such interactions lead to delocalization. However, the presence of electronic absorption bands attributable to individual $TCNQ^-$ molecules, as well as charge transfer transitions between $TCNQ^-$ and both $TCNQ^-$ and $TCNQ^0$ molecules indicate that effects exist which tend to keep the electrons localized on individual sites.

The Hubbard model[15] may be used to account for both delocalization and electron-electron repulsions (Coulomb correlations) associated with the formation of doubly occupied sites. Although originally proposed to treat Coulomb correlations in d and f band metals, the Hubbard model has been successfully applied to the problem of electrons on separate sites. The Hamiltonian is

$$H = \sum_{ij}\sum_{\alpha\beta} t_{ij}^{\alpha\beta} (C_{i\alpha}^{\dagger}C_{j\beta} + C_{j\beta}^{\dagger}C_{i\alpha}) +$$

$$\tfrac{1}{2}\sum_{ijkl}\sum_{\alpha\beta\delta\gamma} \langle i\alpha, j\beta | 1/r | k\delta, l\gamma\rangle C_{i\alpha}^{\dagger}C_{j\beta}^{\dagger}C_{l\gamma}C_{k\delta}$$

where

$$t_{ij}^{\alpha\beta} = \int \phi_{\alpha}^{*}(x-R_i)[-\frac{h^2}{2m}\nabla^2 + V]\phi_{\beta}(x-r_j)dx$$

and

$$\langle i\alpha, j\beta | 1/r | k\delta, l\gamma\rangle = e^2 \int \frac{\phi_{\alpha}^{*}(x-R_i)\phi_{\delta}(x-R_k)\phi_{\beta}^{*}(x'-R_j)\phi_{\gamma}(x'-R_l)}{|x-x'|} dxdx'$$

i,j,k,l are site indices, $\alpha,\beta,\delta,\gamma$ are spin indices, and $C_{i\alpha}^{\dagger}$ and $C_{i\alpha}$ are creation and annihilation operators of an electron at site $\underline{i}$ with spin α. $\phi_a(x-R_i)$ are Wannier type wavefunctions located on site R_i. t_{ij} is the transfer integral, and V stands for the self-consistent potentials acting on the electron. Only terms of the form $\langle ii|1/r|ii\rangle$ are kept, and all other repulsion terms are neglected. Physically, this means that only electron-electron repulsions due to electrons on the same site are considered, and nearest neighbor repulsions are ignored. This procedure is valid since the wavefunctions are Wannier type wavefunctions, and they are expected to be very similar to the LUMO of TCNQ. The Hamiltonian can then be written as

$$H = \sum_{ij}\sum_{\sigma} t_{ij}(C_{i\sigma}^{\dagger}C_{j\sigma} + C_{j\sigma}^{\dagger}C_{i\sigma}) + \tfrac{1}{2}U\sum_{i,\sigma} n_{i\sigma}n_{i\bar{\sigma}}$$

where $U = \langle ii|1/r|ii\rangle$, $n_{i\sigma} = C_{i\sigma}^{\dagger}C_{i\sigma}$, and $\bar{\sigma}$ refers to the opposite

spin. In this model, delocalization effects are accounted for by the t_{ij} term, and localization effects through the U term.

Band Structure in $[Cu(en)_2][TCNQ]_2$. The Hubbard model presented in the previous section does not take site energy differences into consideration. Thus, the model should apply to $[Cu(en)_2][TCNQ]_2$, since, by stoichiometry, all sites have one electron, and presumably have nearly equal energies. Tanaka, et al.[16] have shown that the energy of the charge transfer transition is given by $(U - \sqrt{2}t)$. With this relationship, the energy of the charge transfer transition (1.02 eV), and results of the calculations of $\underline{t}$ for a variety of TCNQ compounds by van Smallen and Kommandeur[17], a value may be estimated for $\underline{U}$. If $\underline{t}$ is taken to be 0.2, a value found in many TCNQ systems, then $\underline{U}$ is estimated to be 1.3 eV.

The effect of $\underline{U}$ is to cause a band gap at the Fermi level. Hubbard[18] has determined that the gap develops for values of $4t/U < 1.15$. $[Cu(en)_2][TCNQ]$ meets this criterion since 4t/U equals 0.62.

Soos and Strebel[19] have determined that the singlet-triplet splitting is given by $4t^2/U$. Using the values of $\underline{t}$ and $\underline{U}$, $\triangle E_{ST}$ is estimated to be 0.12 eV. A system with a $\triangle E_{ST}$ of 0.12 eV would exhibit a magnetic susceptibility on the order of 10^{-5} emu/mole at 300 K. A susceptibility this small could not be detected in the presence of the molar magnetic susceptibility of the S = 1/2 copper complex cation, and in agreement with the experimental observation, TCNQ is not expected to make a detectable contribution to the magnetic susceptibility of $[Cu(en)_2][TCNQ]_2$.

Band Structure of $[Cu(phen)_2][TCNQ]_2$. When there is less than one electron per site, conductivity can occur without the formation of doubly occupied sites. Because of electron transfer from $TCNQ^-$ to the copper(II) complex, $TCNQ^0$ sites are created, and $[Cu(phen)_2][TCNQ]_2$ should exhibit properties consistent with empty-site statistics. The key to understanding the electronic structure and conductivity is provided by the low energy absorption band which arises from $TCNQ^- + TCNQ^0 \rightarrow TCNQ^0 + TCNQ^-$ charge transfer. The presence of this transition reflects a site preference, and when double occupation can be neglected, the difference in site energies dominates the conductivity process.

Soos and Klein[20] have modified the Hubbard model to take into account site energy differences. Essentially, they were able to divide the Hamiltonian into ground and excited state parts. The excited state part consists of the U term due to double occupation. Since conductivity can occur without double occupation of a site when there is less than one electron per site, the excited states can be ignored. Additionally, configuration interaction between the singly occupied and doubly occupied states is neglected. The applicable, modified Hamiltonian is

$$H = \sum_{ij}\sum_{\sigma} E_i C_{i\sigma}^{\dagger} C_{i\sigma} + \sum_{ij}\sum_{\sigma} t_{ij}(C_{i\sigma}^{\dagger} C_{j\sigma} + C_{j\sigma}^{\dagger} C_{i\sigma})$$

where E_i is the energy of site i, and all other symbols have the same meanings as defined above.

The modified Hubbard model yields a band structure in terms of $\underline{t}$ and $\underline{E}$. In the case of t >> E, cosine dispersion curves are obtained. In the case of E >> t, the bands are flat with a gap dependent on $\underline{E}$. Soos and Klein solved this problem for a trimer consisting of two equivalent anionic sites and one neutral site. The percentage of copper(II) in $[Cu(phen)_2][TCNQ]$, as determined from the magnetic susceptibility measurements, shows that, on the average, there is about two-thirds of an electron per site. As an approximation, for this site occupancy, the energy of the charge transfer is 3E, and therefore the site energy difference in $[Cu(phen)_2][TCNQ]_2$ is 0.17 eV (0.5 eV/3). Since the value for ρ from the magnetic susceptibility measurement is subject to error, consider the case of one electron per two sites. For this case the energy of the charge transfer transition is approximately 2E, and the site energy difference is 0.25 eV. Because $\underline{E}$ and $\underline{t}$ are comparable in magnitude in $[Cu(phen)_2][TCNQ]_2$, the bandwidth is still appreciable, and high electrical conductivity and a low activation energy are expected, and observed.[3]

Thus, the energies of the charge transfer bands $TCNQ^- + TCNQ^- \rightarrow TCNQ^0 + TCNQ^{2-}$ and $TCNQ^- + TCNQ^0 \rightarrow TCNQ^0 + TCNQ^-$ yield data which provide an explanation of the magnetic properties of $[Cu(en)_2][TCNQ]_2$ and $[Cu(phen)_2][TCNQ]_2$ in terms of the Hubbard model and its modified variation.

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Figure Captions

Figure 1. Magnetic susceptibility data for $[Cu(en)_2][TCNQ]_2$. The solid line is the best fit of the Curie-Weiss law to the data.

Figure 2. Magnetic susceptibility data for $[Cu(phen)_2][TCNQ]_2$. The solid line is the best fit to the data of a two term equation including a Curie-Weiss component and a pairwise exchange component.

Table I. Electronic Spectral Data[a]

$[Cu(en)_2][TCNQ]_2$		$[Cu(phen)_2][TCNQ]_2$		Comments
RT	77 K	RT	77 K	
365 i	355 i	370 i	370 i	$^2B_{2g} \rightarrow {}^2A_u$
			415 sh	
		500	500	
617 i	612 i	610 i	610 i	$^2B_{2g} \rightarrow {}^2A_u$
		685	685	
		773	765	
			780	
850 i	850 i	875 i	870 i	$^2B_{2g} \rightarrow {}^2B_{1u}$
		1000 sh	985 sh	
1220 vb	1220 vb	1170	1170	$TCNQ^- \rightarrow TCNQ^-$ CT
		~2500 vb	~2500 vb	$TCNQ^- \rightarrow TCNQ^0$ CT

[a]Abbreviations: RT - room temperature; i - intense; sh - shoulder; vb - very broad; CT - charge transfer; band positions given in nm.

FIGURE 1

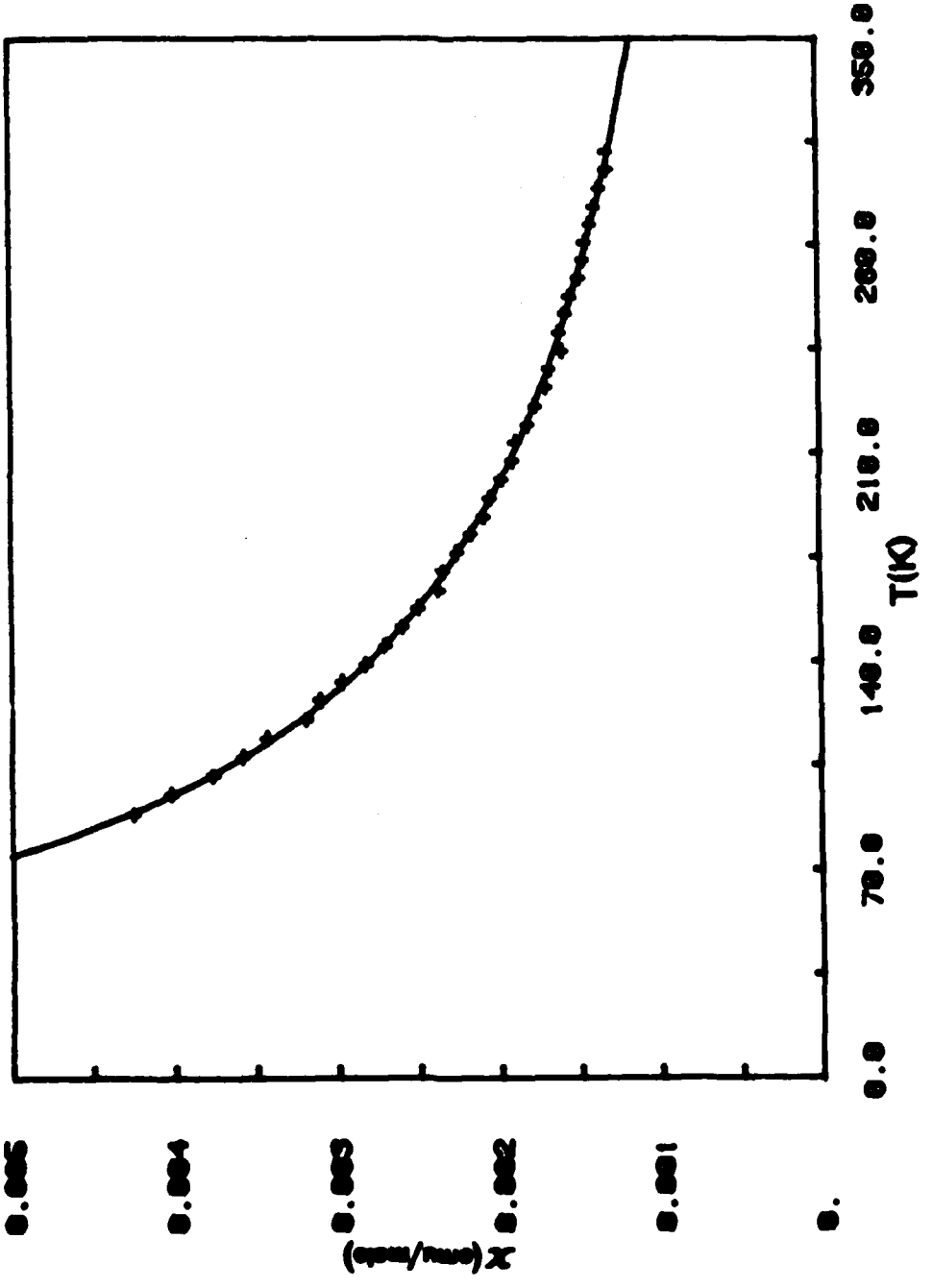
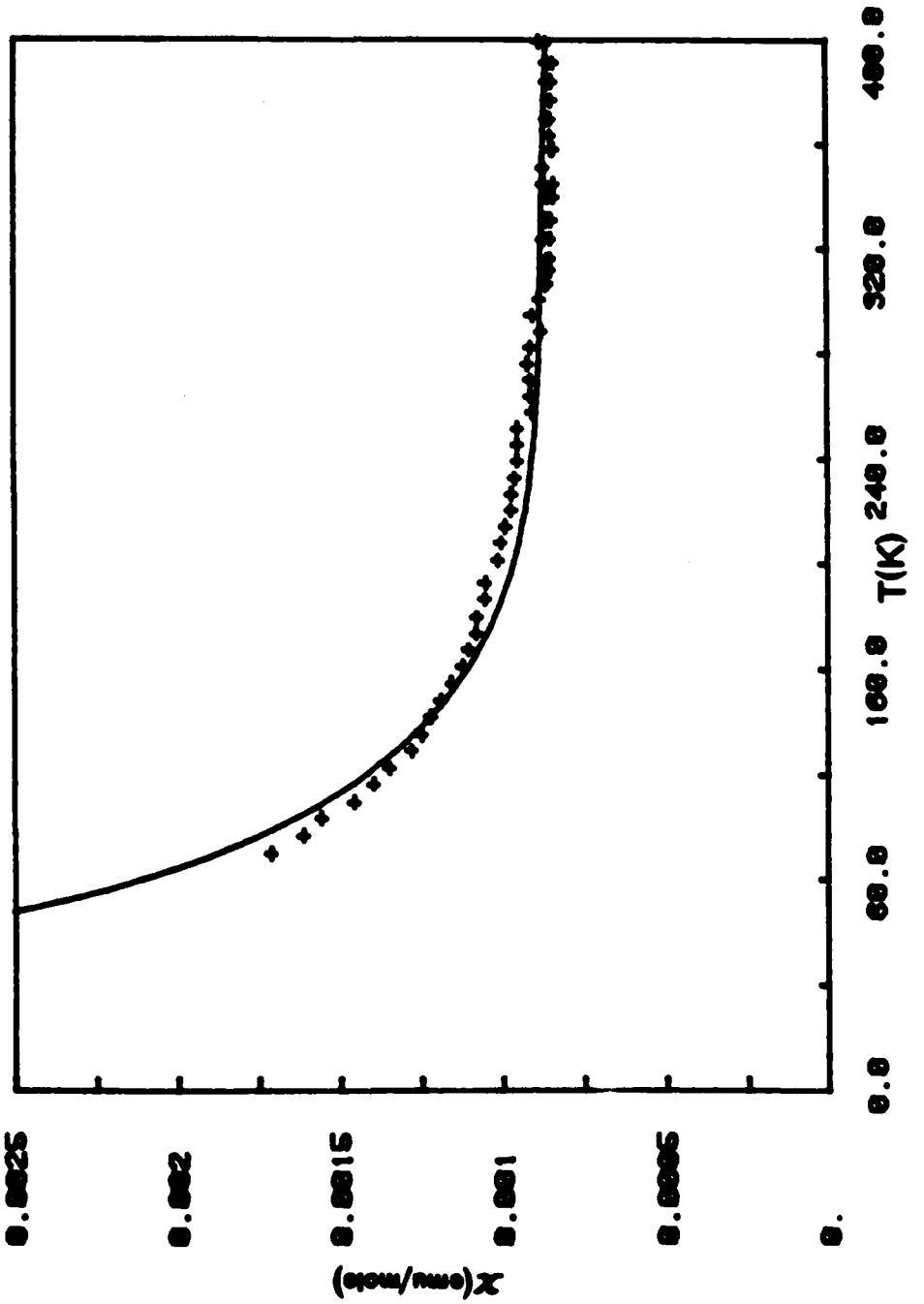


FIGURE 2


0.0
80.0
160.0
240.0
320.0
400.0
T(K)
0.
0.0005
0.001
0.0015
0.002
0.0025
χ(emu/mole)

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